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(58) Field of search

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(54) Organic emulsions for electrodepositing polymeric alloys and copolymers

(57) Organic emulsions have a discontinuous phase which comprises at least two compounds of different structural formula selected from solvent-soluble polymers, oligomers, and monomers dissolved in an organic solvent, and continuous phase which comprises an organic non-solvent for the compounds. The emulsions can be used to coat a conductor (e.g. graphite in the form of a cloth) by immersing the conductor in the emulsion and applying a direct current between the conductor and another electrode so as to cause the discontinuous phase of the emulsion to migrate to the conductor and deposit on it. The conductor is removed from the emulsion and dried, and the deposit is cured if necessary (e.g. if the deposit includes oligomer or monomer).

GB 2 177 707

SPECIFICATION

Improvements in or relating to emulsions for electrodepositing polymeric alloys and co-polymers

This invention relates to emulsions for electrodepositing polymeric alloys and copolymers.

Graphite fibers are of increasing interest for the construction of structural composites because of their very high strength and high stiffness to weight ratios. Performance characteristics of composites depend upon the properties of the materials comprising the composite and the process by which they are combined. Full utilization of the properties of these graphite composites has not been attained because of the weakness of the interphase bonding between the fiber and the matrix. This is due in part to the type of resin used, but also to the wetting of the graphite fiber by the resin.

Generally, graphite fiber or cloth is saturated with the appropriate resin by a dip coating process. Both thermoset and thermoplastic resins have been used to prepare graphite composites. Graphite fibers have also been coated electrophoretically in non-aqueous processes to improve the wetting and impregnation of the graphite by the resin (see U.S. Patent Application Serial No. 717,046, filed March 28, 1985. Attempts to electrophoretically coat graphite fibers from aqueous media have not been very successful because very little resin (only about 1 to 2%) is electrodeposited, and the aqueous medium is deleterious to the fiber.

Accordingly, the present invention resides in a method of making an emulsion from which a polymeric alloy can be electrodeposited which comprises forming a solution in an organic solvent of at least two mutually unreactive compounds selected from organic solvent-soluble polymers, oligomers, and monomers, and mixing said solution with a non-solvent for said compounds.

The invention also includes an emulsion having discontinuous and continuous phases wherein said discontinuous phase comprises at least two compounds of different structural formula selected from organic solvent-soluble polymers, oligomers and monomers, dissolved in an organic solvent, and said discontinuous phase comprises an organic non-solvent for said compounds.

Further, according to the invention is a method of forming a coating on a conductor which comprises immersing said conductor into an emulsion of the last-preceding paragraph applying a direct current between said conductor and an electrode immersed in said emulsion sufficient to cause said discontinuous phase of said emulsion to migrate to said conductor and deposit thereon; removing said conductor from said emulsion; and drying said emulsion.

We have discovered that copolymers and polymeric alloys can be deposited on graphite and other conductors electrophoretically. (A polymeric alloy is a mixture of two polymers; there is no chemical bonding between the two polymers.) Graphite fibers coated by the process of this invention are wetted by the resin better than in prior processes, and there are fewer voids and pores in the resin. We have also been able to achieve resin content values on graphite cloth of from 20 and 50%, far in excess of that achieved by previous processes. As a result of this high resin content, the graphite cloth can be stacked and pressed to form a laminate. Laminates prepared according to the process of this invention have a higher impact strength than do laminates prepared by conventional prepegging methods such as dip coating.

While polymeric alloys have been prepared by other methods such as physical blending, the polymeric alloys prepared according to this invention are structurally different from polymers prepared according to prior processes because the polymers are intimately mixed on a molecular basis.

The starting material in the process of this invention is an emulsion that contains a blend of two or more polymerized or polymerizable compounds in the discontinuous phase. That is, the emulsion consists of a discontinuous phase, which is a solvent containing two or more polymers, oligomers, or monomers dissolved therein, and a continuous phase, which is an organic non-solvent for the polymers, oligomers, or monomers.

Any two or more solvent-soluble polymers, oligomers, or monomers that are compatible can be used to form an emulsion according to this invention. Polymers are preferred to monomers or oligomers as they give better rheological properties on the conductor in that they are less prone to run off. Compounds are considered to be compatible if they are sufficiently miscible so that separate phases do not form. While the compounds can react after they are deposited on the conductor to form a higher molecular weight polymer or a copolymer, they do not react in the emulsion but exist as separate compounds. Any combination of polymers, oligomers, and monomers may be used, such as, for example, 2 polymers, or 2 monomers, or a polymer and a monomer. Also, the compounds may be of different types, such as an epoxy and a polyester, or they may be of the same type but have different structural formulas such as, for example, two dialkyl ethers of bisphenol A having different molecular weights.

- easy to process due to the presence of the lower molecular weight compound. Suitable compounds that can be used in preparing the emulsion include polyesters, epoxies, polysulfones, polyethersulfones, polyimides, polyamide-imides, polyparabanic acids, polycarbonates, elastomer-modified epoxies, polyurethanes, polyethers, polyamide, polyethylene, polytetrafluoroethylene, polypropylene, bismaleimide, triazine, etc. The following pairs of compounds are preferred as they produce coatings with good toughness and high temperature mechanical properties:
- polyimides and epoxies
 - polyamides and epoxies
 - polyimide elastomers and modified epoxies
 - polyamide imides and elastomer-modified epoxies
 - polysulfones and epoxies
 - polyethersulfones and epoxies
 - polysulfones and polyimides
 - polyethersulfones and polyimides
 - polysulfones and polyamide-imides
 - polyethersulfones and polyamide-imides
 - low molecular weight diglycidyl ethers of bisphenol A and high molecular weight diglycidyl ethers of bisphenol A
 - bismaleimide triazine and polyimides, polyamide-imides, epoxies, elastomer-modified epoxies, polysulfones, polyether sulfones, or diglycidyl ethers of bisphenol A
- Two or more compounds may be mixed in any proportion such as, for example, 1 to 99% by weight (based on total solids weight) of one compound and 1 to 99% by weight of the remaining compounds, but it is preferable to use about 20 to about 80% by weight of one compound and about 20 to about 80% by weight of the remaining compounds in order to take advantage of the properties of both compounds in the resulting coating. If one of the compounds is a monomer or an oligomer, a catalyst is preferably included, as is known by those skilled in the art, so that the monomer or oligomer can polymerize once it has been deposited on the conductor. If one of the compounds is a thermosetting polymer, a catalyst is included, as is known to those skilled in the art, in order to cure or cross-link the polymer once it has been deposited on the conductor.
- The solvent is an organic solvent, and it is a solvent for a sufficient amount of the compounds to result in the formation of the emulsion. Suitable solvents include methylene chloride, acetone, dimethylformamide, 2-methylpyrrolidone, 1,1,2-trichloroethane, dimethylsulfoxide, xylene, and decahydronaphthalene. Other suitable solvents will no doubt occur to those skilled in the art.
- The non-solvent is also organic and is a non-solvent for a sufficient amount of the polymers, oligomers, and monomers to result in the formation of the emulsion. The non-solvent can be miscible or immiscible with the solvent, but it is preferably miscible with the solvent as this tends to result in a coating that is more solvent-free. If the non-solvent is immiscible with the solvent, it may be necessary to include an emulsifier such as a tertiary amine in the emulsion to aid in its formation, as is known in the art. Non-solvents that can be used in forming an emulsion according to this invention include acetonitrile, diamethylformamide, acetone, and other ketones such as methyl ethyl ketone, methyl isobutyl ketone, and cyclohexanone. Whether a particular organic liquid is a solvent or a non-solvent will depend upon the particular polymeric compounds used in forming the emulsion.
- Desirably, the weight ratio of non-solvent to solvent should be from 2 to 10 as ratios outside this range tend to result in the deposition of less material or produce a less stable emulsion; the preferred weight ratio of non-solvent to solvent is from 3.5 to 4.5. Emulsion containing from about 0.5 to 1.5 wt. % solids based on the total emulsion weight have proved to be especially convenient. If less than 0.5% solids are present, the electrodeposition process will still work but it will take a rather long time, and if more than 1.5% solids are present, the emulsion tends to be less stable; preferably, the per cent solids is from 0.9 to 1.1.
- While an emulsifier is preferably not present, from 0.5 to 1 wt. % (based on solids) of an emulsifier can be used when the solvent and non-solvent are immiscible or when the emulsion does not readily form. Preferably, the amount of emulsifier is from 0.1 to 0.3% by weight.
- In preparing the emulsion, the solid materials are dissolved in the solvent and the resulting solution is mixed with the non-solvent. If it is desirable to have the different polymeric materials in different droplets in the emulsion, they are dissolved in separate solvents and the separate solvents are added separately to the non-solvent. It may be necessary to heat and stir the mixture in order to emulsify the components.
- The conductor can be of any shape including a flat surface, individual fibers, mat, roving, or woven cloth. It can also be of any material that conducts electricity including metals, graphite, boron, and silicon. Graphite fibers that are woven into cloth are the preferred conductor because they have a high specific modulus and a high specific strength which makes them very useful in

the conductor and an electrode in contact with the emulsion. The conductor can be either the anode or the cathode, depending upon the particular materials used, but most commonly, the conductor will be the anode. A voltage of about 1 to about 500 volts is suitable. The current is applied until the desired thickness of coating on the conductor has been achieved or until additional material will not deposit on the conductor. The conductor may be coated in either a continuous or batch process.

After the conductor is coated, it is removed and dried. If the conductor is coated with a thermoplastic material, it is heated to fuse or melt the thermoplastic and form a smooth coating on the conductor. If the conductor has been coated with a monomer, oligomer, or reactive or cross-linkable polymers, it is heated to polymerize, react, or cross-link the polymeric material in the coating.

If a laminate is to be made, the conductor is preferably a woven cloth. The process of this invention will deposit sufficient resin on the cloth to permit the cloth to be used directly in forming the laminate. Sheets of the cloth are stacked, heated, and pressed to form the laminate. In addition to preparing laminates, the process of this invention can also be used to make coatings on metal surfaces, as insulation on metals, and as wire enamel on wires. It can also be used to coat graphite fibers for use in making articles by filament winding.

The invention will now be illustrated with reference to the following Examples:

20 EXAMPLE 1

An emulsion was prepared by adding a solution of 1360 g N-methylpyrrolidone (NMP) and 61.48 g of a low molecular weight or a high molecular weight polyethersulfone sold by ICI Chemical Corporation under the trade designations "Vitrex 100P" or "Vitrex 300P," respectively, from a separator funnel to 4788 g of stirred acetone. Graphite cloth 7-1/4"X9" was immersed into the emulsion so that the immersed portion was 7-1/4"X8". The cathode was an expanded nickel screen 9" longX4-3/4" wide. Electrode separation was 3". A potential was applied for varying times and the coated cloth was dried in an oven using the following schedule: 5 min 75°C+5 min 75-100°C+5 min 100-125°C+5 min 125-150°C+10 min 150-180°C. The results of this electrocoating procedure are shown in Tables 1 and 2.

TABLE 1 - "VICTREX 100P" ON GRAPHITE CLOTH

Graphite Cloth	Time (Mins) & Voltage (dc)	Current mA	Coulombs	Resin Content, wt. %
A	10 50-150	--	--	43
B	8 150	160-155	92	39
C	10 1/2 150	162-160	124	38
D	10 150	156-150	116	31
E	8 150	160-158	100	22
F	9 150	165-160	109	33
G	10 150	170-168	122	30
H	12 150	180-178	141	26
I	9 150	100-90	59	40
J	11 150	98-90	65	40
K	10 1/2 150	90-83	60	35
L	14 150	85-75	72	35
M	13 1/2 150	98-86	79	33
N	14 150	100-87	93	24

TABLE 2 - "VICTREX 300P" ON GRAPHITE CLOTH

Graphite Cloth	Time (Mins) & Voltage (dc)	Current mA	Coulombs	Resin Content, wt. %
A	8 150	58-52	31	31
B	9 150	55-49	32	30
C	11 150	55-48	39	33
D	9 1/2 200	73-60	45	37
E	10 200	69-56	45	36
F	8 200	82-73	46	34
G	9 200	79-69	49	29
H	11 200	78-64	58	28
I	13 200	75-61	64	24
J	11 250	92-72	66	24
K	13 300	110-86	91	23
L	7-200	72-66	33	47
M	7 1/2 200	69-64	34	40
N	6 250	86-79	34	41
O	6 1/2 250	85-76	35	38
P	7 250	81-74	36	32

The graphite cloth was stacked in the warp and fill direction such that the stacking symmetry was maintained about the center of the laminates. Specimens were cut in the warp and fill directions relative to the outside ply in all applicable cases. The coated graphite cloth described in Tables 1 and 2 was converted to a laminate by stacking the 6"X6" pieces of coated graphite cloth, 14 plies in all, alternately in a warp and fill direction and placing them in a cold press. A pressure of 1,000 psi was applied and the press was heated to 450°F (about 1/2 hr). The laminates were held at 450°F and 1,000 psi for 1 hr and were cooled to room temperature under pressure with cold water (approximately 1 hr). Impact tests were run on the laminates by machining specimens parallel to the

TABLE 3 - Energy (in-lb/in²)

Components	Initiation		Total	
	Fill Direction	Warp Direction	Fill Direction	Warp Direction
Polysulfone - "300P"	180	100	900	580
Commercial System	440	240	920	775
Polysulfone - "100P"	180	265	1010	1140

As can be seen from Table 3, graphite-polyethersulfone "100P" composite was tougher than the Commercial System in both directions since the total energy absorbed is higher. (The Commercial System is sold by Hercules, and is believed to be type AS4 woven graphite fiber impregnated with N,N,N',N'-tetraglycidyl ether of diamino diphenyl methane sold by Ciba-Gigy under the trade designation "MY720" cured with diamino diphenyl sulfone.)

Weight loss as a function of exposure temperature was measured for the three systems. The following table gives temperatures that resulted in a 1% weight loss. Measurements were conducted on thermogravimetric analysis equipment.

Laminate Materials	Temperature
"300P" + graphite cloth	300°F
"100P" + graphite cloth	320°F
Commercial System	270°F

From the above table, it is clear that laminates made from polyethersulfones ("100P" and "300P" possess superior thermal stability over the Commercial System so widely used in the aerospace industry.

EXAMPLE 2

Dimethylformamide (540g) was heated to 80°C and 120 g of "Victrex 100P" was slowly added (about 10 g/min) and stirred until it had all dissolved (about 10 minutes). At this point, 280g of "MY-720," heated to 80°C, was added, and stirring was continued at that temperature for 45 minutes. The dark amber solution was cooled to room temperature. A homogeneous solution was obtained as a first composition. This composition contained a weight ratio of epoxy to polyethersulfone of (2:1), and had a solids content of 50%.

A second composition was prepared as described above except that the weight ratio of epoxy to polyethersulfone was 1 to 2.33. The composition was as follows:

Dimethylformamide (DMF) = 690 g
 "Victrex 100P" = 280 g
 Diaminodiphenyl sulfone = 60 g
 "MY-720" = 120 g

Milky colored emulsions were prepared by diluting the solutions having the first and second compositions with DMF and adding them slowly from a separatory funnel to a stirred acetone solution. The compositions of the various emulsions are shown in Table 4.

TABLE 4						
No.	Solution Having First Composition (g)	Solution Having Second Composition (g)	DMF (g)	Acetone (g)	Non-Solvent to Solvent Ratio	Solids Wt. %
1	5		73	174.5	2.31	0.99
2	"		68	179.5	2.54	"
3	"		63	184.5	2.81	"
4	"		58	189.5	3.13	"
5	"		53	194.5	3.50	"
6	"		48	199.5	3.95	"
7	"		43	204.5	4.49	"
8	"		33	214.5	6.04	"
9		5	58.5	135.1	2.19	1.0
10		"	50.5	143.1	2.70	"
11		"	42.5	151.1	3.30	"
12		"	34.5	159.1	4.24	"
13		"	26.5	167.1	5.66	"

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Electrodeposition was carried out at constant voltage in a Pyrex glass beaker. The anode was an aluminum rod (Type 6061T6) 0.250" in diameter and 8" long which was immersed in the emulsion to a depth of 2". A circular nickel screen designated (10Ni 12-2/0) served as the cathode and was placed around the anode such that the electrode separation was 1".

Aluminum rods were immersed in each of the emulsions and 300 Vdc were applied for 1 minute. The coated rods were dried 5 minutes at 100°C + 5 minutes 100-150°C and weighed. The results are given in Table 5.

TABLE 5	
No. *	Weight of Electrodeposited Coating, mg
1	39
2	46
3	51
4	55
5	55
6	55
7	56
8	48
9	52
10	51
11	63
12	55
13	45

*These numbers correspond to those in Table 4.

60 EXAMPLE 3

Emulsions A and B were used to coat the cloth. The compositions are as follows:

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Ingredient	Emulsion A(g)	Emulsion B(g)
5 Solution having first composition	125	—
Solution having second composition	—	150
DMF	1325	1275
10 Acetone	3862.5	4533

Graphite cloth designated "A370-5H" from Hercules Corp., about 20 mils thick, was cut into 7"X9" pieces and immersed into the emulsions in a polyethylene container. The cathodes were of the same nickel screen material described in Example 1. The cathode was 5" wide and 8-1/2" long and the electrode separation was 3". The data for the electrocoating of the graphite cloth is shown in Table 6.

TABLE 6					
No.	Voltage	Time, (Mins)	Current (mA)	Coulombs	Resin Content of Coated Graphite (g)
1	300	10	160-95	104	24
2	"	13	160-80	108	22
3	"	18	110-55	97	15
4	"	36	80-50	144	15
5	"	10	165-120	127	32
6	"	17	160-65	128	26
7	"	25	100-50	128	17
8	"	34	60-40	128	11
9	"	10	240-110	122	30
10	"	22	140-45	123	26
11	"	32	80-40	122	16
12	"	52	50-25	143	8
13	"	10	220-110	113	30
14	"	15 1/2	160-95	114	23
15	"	24 1/2	110-40	114	17
16	"	50	70-25	146	15

EXAMPLE 4

An emulsion was prepared which consisted of 150 g of a polyimide sold by Upjohn Chem. Co. as a 22% solution in NMP under the trade designation "PI-2080," 130 g of N-methyl pyrrolidone, and 4500 g of acetone. Graphite cloth was electrocoated with this emulsion. The results are presented in Table 7.

TABLE 7

No.	Voltage	Time	Current (mA)	Coulombs	Resin Content of Coated Graphite (wt.%)
1	100	35 sec	170-145	6.5	2.0
2	"	7 min	150-120	77	24
3	"	10 "	140-110	98	28
4	"	12 "	130-100	118	31
5	"	14½ "	130-100	147	31
6	"	20 "	125-100	156	30
7	"	20½ "	125-100	167	24
8	"	22 "	125-100	188	21
9	"	35 "	110- 80	214	18
10	"	8 "	150-120	88	27
11	"	14 "	130- 95	113	39
12	"	14 "	130- 95	115	32
13	"	16 "	130- 95	127	31
14	"	17 "	125- 90	133	27
15	"	17½ "	130- 90	145	23
16	"	21½ "	110- 80	164	18

The coated graphite was dried in an oven for 5 minutes at 70°C, 5 minutes at 70 to 100°C, 5 minutes at 100 to 150°C and 5 minutes at 150-200°C.

30 EXAMPLE 5

Polymer blends of different polymers were prepared by dissolving the polymers in a suitable solvent. Table 8 gives these compositions.

TABLE 8

Ingredient	A	B	C	D
"MY-720"	10 g		10	g
"PI-2080"	2.5 g	12 g	5 g	5 g
"Victrex 100P"		3 g		5 g
Bismaleimide resin				5 g
DMF	34 g	35 g	23 g	85 g

Using the blends in Table 8 emulsions were prepared by adding the blends to acetone. The composition of these emulsions is given in Table 9.

TABLE 9				
Ingredient	Emulsion A	Emulsion B	Emulsion C	Emulsion D
Solution A	10 g			
" B		10 g		
" C			8 g	
" D				12 g
DMF	55 g	25 g	58 g	26 g
Acetone	181 g	82 g	191 g	85 g

Aluminum rods were electrocoated with these emulsions. The electrocoating procedure is described in Example 3. A voltage of 300 Vdc was applied for 15 to 30 seconds. In all cases a heavy coating was deposited on the anode.

EXAMPLE 6

Using the electrocoated graphite cloth prepared in Example 4, a laminate was prepared. The graphite cloth was stacked in the warp and fill direction such that the stacking symmetry was maintained about the center of the laminates. Specimens were cut in the warp and fill directions relative to the outside ply in all applicable cases.

The 6"X6" pieces of the coated cloth, 14 plies in all, were stacked alternately in a warp and fill direction and placed in a preheated press (590°F). Pressure (4500 psi) was applied and the temperature was raised to 670°F. Upon reaching this temperature (about 10 minutes) the laminate was held at this temperature for another 5 minutes. The laminate was allowed to cool under pressure to a temperature of 590°F (about 15 minutes) and further cooled to 300°F, at which point the cooling water was turned on and further cooled to room temperature.

EXAMPLE 7

Another laminate was prepared using the electrocoated graphite cloth prepared in Example 3. The graphite cloth was stacked in the warp and fill direction such that the stacking symmetry was maintained about the center of the laminates. Specimens were cut in the warp and fill directions relative to the outside ply in all applicable cases. Fourteen plies of 6"X6" cloth were stacked alternately in the warp and fill direction. The stack was placed in a cold press and pressure (1000 psi) was applied. The press was heated to 350°F (30 minutes) and the laminate held for 2 hrs at temperature and pressure before cooling with water to room temperature. The laminates prepared in Examples 6 and 7 were tested and the results shown in Table 10.

TABLE 10 - Energy (in-lb/in ²)				
Components	Initiation		Total	
	Fill	Warp	Fill	Warp
	Direction	Direction	Direction	Direction
Upjohn "2080"	90	230	740	860
"MY-720" - "100P"	160	185	690	590

As shown in Table 10, crack initiation energy for the two systems is similar to the Commercial System, but total energy to failure is lower than the Commercial System. This may be due to higher percentage of voids and lower resin contents found in these laminates. Table 11 lists volume percentages of reinforcement, matrix and voids.

TABLE 11			
Laminate Type	Reinforcement	Matrix	Void
	Volume % (ml)	Volume % (ml)	Volume % (ml)
1. Polyethersulfone, "100P" and graphite cloth	58.0	38.0	4.0
2.. Polyethersulfone, "300P" and graphite cloth	64.5	32.5	3.0
3. Upjohn "2080" and graphite cloth	68.0	24.6	7.4
4. "My-720", Polyethersulfone "100P" and cured with	70.0	21.0	9.0
5. Commercial System	61.0	36.0	3.0

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CLAIMS

1. A method of making an emulsion from which a polymeric alloy can be electrodeposited which comprises forming a solution in an organic solvent of at least two mutually unreactive compounds selected from organic solvent-soluble polymers, oligomers, and monomers, and mixing said solution with a non-solvent for said compounds.
2. A method according to claim 1, wherein the solution consists of at least two separate portions each containing at least one of the compounds which are structurally different and said portions of said solution are mixed separately with the non-solvent for said compounds.
3. An emulsion having discontinuous and continuous phases wherein said discontinuous phase comprises at least two compounds of different structural formula selected from organic solvent-soluble polymers, oligomers and monomers, dissolved in an organic solvent, and said discontinuous phase comprises an organic non-solvent for said compounds.
4. An emulsion according to claim 3, wherein at least one of the compounds is thermosetting and at least one of the compounds is thermoplastic.
5. An emulsion according to claim 3 or 4, wherein the discontinuous phase consists of droplets, a majority of which contain only one of the compounds.
6. An emulsion according to claim 3 or 4, wherein the discontinuous phase consists of droplets, a majority of which contain more than one of the compounds.
7. An emulsion according to claim 3, 4, 5 or 6, wherein the compounds are co-reactive during curing.
8. An emulsion according to any of claims 3 to 7, wherein the compounds are a pair of compounds selected from polyimides and epoxies, polyamide-imides and epoxies, polyimides and elastomer-modified epoxies, polyamide-imides and elastomer-modified epoxies, polysulfones and epoxies, polyethersulfones and epoxies, polysulfones and polyimides, polyethersulfones and polyamide-imides, diglycidyl ethers of different molecular weight, and bismaleimide triazine and polyimide, polyamide-imide, epoxy, elastomer-modified epoxy, polysulfone, or polyethersulfone.
9. An emulsion according to any of claims 3 to 8 wherein the solvent and non-solvent are miscible.
10. An emulsion according to any of claims 3 to 9, wherein the weight ratio of the non-solvent to the solvent is from 2 to 10, and the weight per cent solids in said emulsion based on emulsion weight is from 0.5 to 1.5.
11. An emulsion according to claim 10 wherein the weight ratio of the non-solvent to the solvent is from 3.5 to 4.5, and the weight percent solids in the emulsion based on emulsion weight is from 0.9 to 1.1.
12. An emulsion according to any of claims 3 to 10, wherein the discontinuous phase comprises from 20 to 80% by weight based on total solids of compound and about 20 to about 80% by weight of a second compound.

phase of said emulsion to migrate to said conductor and deposit thereon; removing said conductor from said emulsion; and drying said emulsion.

14. A method according to claim 13, wherein the conductor is heated to cure polymeric material deposited thereon.

5 15. A method according to claim 13 or 14, wherein the voltage of the direct current is from 1 to 500 volts.

16. A method according to claim 13, 14 or 15, wherein the conductor is in the form of woven graphite fibers.

10 17. A method according to claim 16, wherein the woven graphite fibers with polymeric material deposited thereon are stacked and heated under pressure to form a laminate.

18. A method of making an emulsion from which a polymeric alloy can be electrodeposited and substantially as described herein with particular reference to Examples 1 to 5 of the foregoing Examples.

15 19. A method of forming a coating on a conductor and substantially as described herein with particular reference to Examples 1 to 5 of the foregoing Examples.

20. A method of making a laminate substantially as described herein with particular reference to Examples 6 and 7 of the foregoing Examples.

21. Emulsions when made by a method as defined in claims 1, 2 or 18.

22. Coated conductors when made by a method as claimed in any of claims 13 to 16 or 19.

20 23. Laminates when made by a method as claimed in claim 17 or 20.